

Recovery of metal values from a mixture of spent lithium-ion batteries and nickel-metal hydride batteries

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Abstract

A novel process for the recovery of metal values from a mixture of spent lithium-ion batteries (LIBs) and nickel-metal hydride (NiMH) batteries is presented. The iron shells of spent batteries were firstly dismantled using a specially designed dismantling machine. Then after the separation of aluminum substrate and electrolyte and the subsequent heating treatment, iron shells and metal-mesh substrate in the dismantled substances were effectively separated with a sieve. The powder residues including LiCoO₂, copper oxides, metal nickel and hydrogen storage alloy and their oxides were dissolved using 3 mol L⁻¹ H₂SO₄+3 wt.% H₂O₂ at 70 °C, S/L=1:15 for 5 h. Finally, rare earths (RE) were precipitated as sodium RE double sulfate, copper was extracted as CuSO₄ with 10 wt.% Acorga M5640 at pH=1.5–1.7, cobalt and nickel were extracted as their sulfates with 1 M Cyanex272 at pH=5.1–5.3 and 6.3–6.5, respectively. The experimental results showed that the recovery exceeded 94% for all metal values.

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1. Introduction

Lithium-ion batteries (LIBs) and nickel-metal hydride (NiMH) batteries have played a leading role in the portable secondary battery market since their commercialization (Köhler et al., 2004; Nishi, 2001). Because metal values such as nickel, cobalt, copper and rare earths (La, Ce, Pr and Nd, shown as RE) and corrosive electrolytes are contained in both batteries, recycling of spent LIBs, and NiMH batteries has become an urgent matter from the viewpoint of environmental protection and resource conservation.

Up to now, some typical hydrometallurgical and pyrometallurgical processes for the recycling of spent LIBs and NiMH batteries have been reported or patented (Han and Nan, 2005; Espinosa et al., 2004); Co, Li and Cu are usually recovered from spent LIBs (Zhang et al., 1998a,b; Kim et al., 2004; Lin et al., 2003; Tanii et al., 2003), and Co, Ni and RE or Fe-based alloy are reclaimed from spent NiMH batteries (Kleinsorgen et al., 2000; Pietrelli et al., 2002; Zhang et al., 1999, 1998a,b). In these reported hydrometallurgical process, di-(2-ethylhexyl) phosphoric acid (D2EHPA), bis-(2,4,4-tri-methyl-pentyl) phosphinic acid (Cyanex272), trioctylamine (TOA), diethylhexyl phosphoric acid (DEHPA) or 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) were usually used as extractants to separate the metal values. In addition, using spent batteries to prepare LiCoO₂ electrode materials (Lee and Rhee, 2003; Contestabile et al.,

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2001; Nan et al., 2004), metal hydride electrodes (Wang et al., 2002; Prickett et al., 2001) and Ni–Co alloy (Lupi and Pilone, 2002) were also investigated.

Based on hydrometallurgical processes, we investigated methods for recycling spent LIBs and spent NiMH batteries, and metal values and electrode materials including Co, Li, Ni, Cu, LiCoO₂ and Ni(OH)₂ were obtained (Nan et al., 2004, 2005, 2006). In the recycling process of spent LIBs (Nan et al., 2005), oxalate and Cyanex272 were employed to separate Co and subsequently synthesize LiCoO₂ electrode material, most copper was left as metal strip and the small amount of Cu dissolved with H₂SO₄ was extracted with Acorga M5640 (hydroxy-oxime derivative). In the recycling process of spent NiMH batteries (Nan et al., 2006), the recovered NiSO₄+CoSO₄ solution was employed to synthesize Ni(OH)₂ electrode material after the separation of outer shells, RE and impurities. However, it was also noticed that mixing of these two spent batteries was unavoidable during collection, and dealing with the separation of the mixed spent batteries was relatively difficult in the practical treatment process. Because more elements would be involved in the target batteries, and the cost and large-scale feasibility should also be particularly considered for a practicable process, those proposed processes that solely reclaimed spent LIBs or spent NiMH batteries were unusable for the combined spent batteries and thus must be readjusted.

Considering that metal values of Co and Cu and organic LiPF₆ electrolyte, and Ni, Co and RE and corrosive alkaline electrolyte are contained in LIBs and NiMH batteries, respectively, and some species such as their electrolytes can react with each other, a novel process was developed to reclaim a mixture of spent LIBs and NiMH batteries. In this paper, the pretreatment of spent batteries, and the recovery of metal values including RE, Co, Cu and Ni from a mixture of spent LIBs and NiMH batteries are all presented.

2. Experimental

2.1. Materials

The cylindrical spent LIBs and NiMH batteries used in this work were kindly provided by Great Power Battery Co. LTD. The positive electrodes of spent NiMH batteries were comprised of formed nickel substrate and Ni(OH)₂ active material, the negative electrodes consisted of AB₅-type hydrogen storage alloy powders and iron or copper-mesh substrate. In spent LIBs, LiCoO₂ and carbon powders were pasted on aluminum foil and copper foil as positive and negative electrodes, respectively. The contents of the substances in the two batteries

were similar to those of the commercial batteries with the same size in the market.

A half of spent LIBs and NiMH batteries were used. The commercial extractions Acorga M5640 and Cyanex272 (di-(2,4,4 trimethyl pentyl) phosphoric acid) were used as extractants for the separation of Cu²⁺, Ni²⁺ and Co²⁺. Kerosene was used as diluent both for Acorga M5640 and Cyanex272. All reagents were utilized as-received without further purification.

2.2. Analysis methods

The concentrations of various metallic ions in the initial solutions and subsequent resultants were all determined by using atomic absorption spectrophotometer (model AA320, China). The pH values of the aqueous solutions were measured with a pH/mV meter (Model DF-801, China).

3. Results and discussion

3.1. Separation of the outer iron shells of spent batteries

The desirable metal values, i.e. Ni, Cu, Co and RE, were contained in the inner part of spent batteries, in order to separate these elements out, respectively, the outer iron shells of spent batteries must be firstly dismantled and separated. An especially designed dismantling machine was used to accomplish this. The digital image of the dismantled substances is shown in Fig. 1a. It can be seen that the inner substances of spent batteries were peeled off after the dismantling of battery shells, which is very usable to the next separating treatment.

It was found that self-ignition of the dismantled substance occurred easily due to the short circuit of two electrodes and the contact of hydrogen storage alloy powders with moist air. In addition, the electrolyte of spent LIBs, i.e. lithium phosphohexafluoride (LiPF₆) dissolved in organic solvent, could also react with water and produce dangerous gases such as pentafluoroarsenic, pentafluorophosphate and hydrogen fluoride. So, the dismantled substances were immediately poured into a plastic container with alkaline solution after the dismantling treatment. The electrolyte of NiMH batteries is corrosive alkaline solution, while an acidic solution is produced from LIBs when its organic electrolyte contacted with water. Because the alkaline solution had a high concentration, some alkaline solution would be left after the acid–base neutralization reaction, thus, some of the aluminum substrates of LIBs could also be dissolved. The recovery value of aluminum is negligible, and the introduction of Al³⁺ in the next dissolving step would go against the separation of metal values (Nan

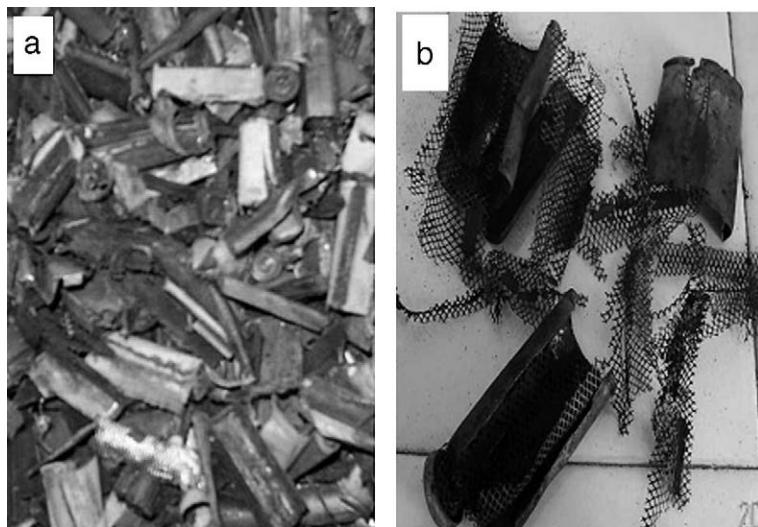


Fig. 1. Digital images of the dismantled substances of spent LIBs and NiMH batteries (a) and the separated iron shells and mesh substrate (b).

et al., 2004), therefore, the aluminum substrates of LIBs were dissolved by adding 10 wt.% NaOH solution. Experimental results showed that over 98% of aluminum could be separated when a solid-to-liquid (S/L) ratio of 1:10 was used for 5 h at room temperature, and LiCoO₂ flakes coated on aluminum foil were left in the residues after filtration of the aqueous solution.

After the removal of electrolyte and the aluminum substrate of LIBs, the residues were heated in a furnace (Nan et al., 2006). It was indicated that the separator, plastic parts and organic adhesive could be burnt off with a heating temperature of 580–630 °C for 5 h in air, and the exhaust gas could be innocuously flowed through a filtration device. At the same time, the active material, i.e. hydrogen storage alloy powders on the metal hydride electrodes of NiMH batteries, were brushed off from their metal-mesh (i.e. iron-punched and copper-mesh) substrate; the active material of nickel electrodes, their formed-nickel substrate, and copper substrate of LIBs were also pulverized during the heating treatment. This is very important to the next step, which means the iron shells and metal-mesh substrate could be separated easily from the powder residues with a sieve with 1.5 mm aperture. Even if a little of powder was left on the crusts or metal-mesh substrate, watering was still useful. The separated iron shells and mesh substrate is shown in Fig. 1b.

3.2. Recovery of rare earths with chemical deposition

To match the next separation operation and based on our previous studies (Nan et al., 2004, 2005, 2006), the powder residues obtained above, including LiCoO₂, metal nickel, copper and hydrogen storage alloy and their oxides, were

dissolved using 3 mol L⁻¹ H₂SO₄ and 3 wt.% H₂O₂, 70 °C and solid-to-liquid (S/L) ratio of 1:15. The effect of reaction time on the dissolution of Co, Ni, and Co is presented in Fig. 2. It is seen that the dissolution of powder residues was enhanced with the increase of dissolving time, and about 90% Co, Ni, and Co could be leached out after 5 h. In addition, it was also found that the dissolution of mixed RE was over 99.5% in 5 h under such dissolution conditions. The insoluble material could be put in the posterior batch. So, the dissolving time of 5 h was chosen in the given process.

The contents of main elements contained in the product solution are given in Table 1. More than 99.5% iron was separated using the sieving method above, while the main elements in the product solution are the high value target metals. This is very convenient and economical

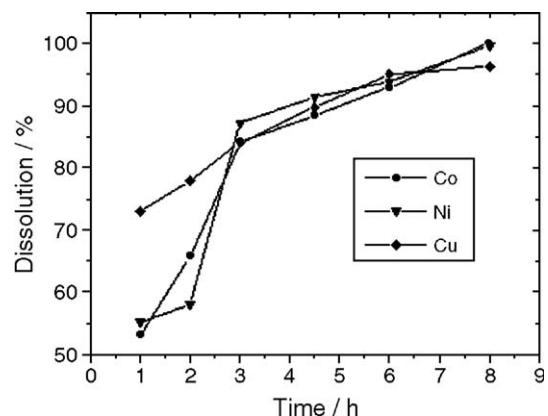


Fig. 2. Effect of reaction time on the dissolution of Co, Ni, and Cu using 3 mol L⁻¹ H₂SO₄ and 3 wt.% H₂O₂ at 70 °C and S/L=1:15.

Table 1

Contents of main elements in the dissolution product solution of spent LIBs and NiMH scraps obtained with 3 mol L⁻¹ H₂SO₄ and 3 wt.% H₂O₂

Elements	Cu	Fe	Co	Ni	Mn	Li	Al	La	Ce	Pr	Nd
Contents (g L ⁻¹)	4.30	0.054	16.7	11.0	0.53	1.35	2.46	2.39	1.01	0.11	0.41

with respect to the next separation of metal values. Practically, although the iron content in the product solution changed for the different batches, at least over 98% iron could be separated. In addition, with the addition of H₂O₂ in the acidic dissolving solution, Fe²⁺ was easily oxidized to Fe³⁺, and then separated as a precipitate by increasing the solution pH above 4.5 in the next treatment.

Rare earths were recovered by adjusting the pH of the dissolution solution, precipitating insoluble double RE sulfate salts (Kleinsorgen et al., 2000; Pietrelli et al., 2002; Nan et al., 2006). A solution mixture of 6.5 wt.% NaOH + 3.5 wt.% Na₂CO₃ was used to adjust the pH. The influence of pH on the precipitation of La and Ce is shown in Fig. 3. It can be seen that the residual contents of La and Ce in solution decreased dramatically with increase of pH to 1.2. Over 94% of La and Ce (also for Pr and Nd) precipitated when pH approached 1.6. Because the other elements did not precipitate, the insoluble double RE sulfate salts could be recovered by filtration.

3.3. Separation of Cu, Co and Ni with solvent extraction

After the separation of RE from the dissolving solution, the metal values of Cu²⁺, Co²⁺ and Ni²⁺ were left. Acorga M5640 was firstly chosen as extractant for the separation of Cu²⁺ (Nan et al., 2004, 2005; Alguacil et al., 2002), and then Cyanex272 was used for extracting Co²⁺ and Ni²⁺ under different pH values (Zhang et al., 1998a,b; Nan et al., 2004, 2005).

To obtain the optimum conditions for separating Cu²⁺ with Acorga M5640, several extraction factors, includ-

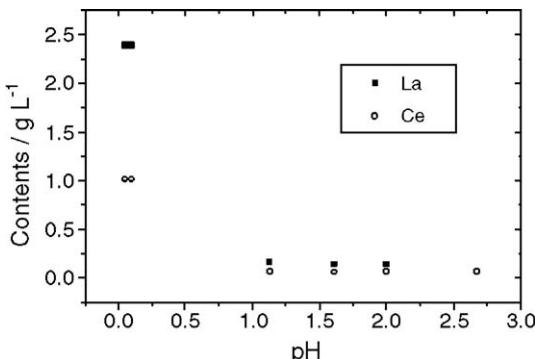


Fig. 3. The residual contents of La and Ce in the dissolution product solution with the increase of pH value.

ing extractant concentration, reaction temperature and time, pH value and O/A phase ratio were investigated. A solution mixture of 6.5 wt.% NaOH + 3.5 wt.% Na₂CO₃ was used to adjust the pH value. Each of the above factors was studied with different levels while the other factors were fixed. It was found that these factors had similar effects on the extraction of Cu²⁺ in this solution compared with Cu²⁺ separation from the mixed solution of Cu²⁺ and Co²⁺ (Nan et al., 2005). Therefore, 10 wt.% Acorga M5640 at 1:1 (O/A) phase ratio, room temperature and 10 min of contact time was selected to separate Cu²⁺.

The extraction behavior of copper with 10 wt.% Acorga M5640 at different pH values is shown in Fig. 4. It can be seen that 98.5% extraction of Cu²⁺ could be obtained when pH value of 1.5–1.7 was used; the loaded organic was stripped with 2 M H₂SO₄ at 1:1 (O/A) phase ratio, room temperature, and 1 min of contact time. At the same time, because of the relatively high contents of Co²⁺ and Ni²⁺ in the pregnant leach solution, a large proportion of Co²⁺ and Ni²⁺, i.e. about 16.3% and 5.6%, was extracted with Cu²⁺, in spite of the high selectivity for copper with Acorga M5640. Therefore, the strip product solution was subjected to the same extraction operations until the target CuSO₄ solution reached the expected purity.

After the separation of Cu²⁺, the pH of the solution was then adjusted to 5.1–5.6; over 95% of the remaining Al³⁺, Fe³⁺, Cu²⁺ and RE was precipitated, which means the contents of these elements were reduced to very low

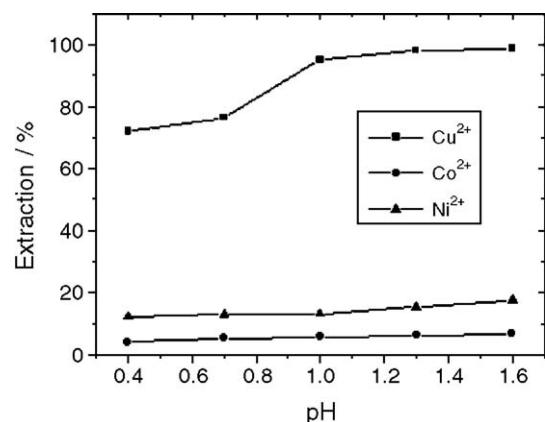


Fig. 4. The extraction of Cu²⁺, Ni²⁺ and Co²⁺ with 10 wt.% Acorga M5640 at different pH values.

Table 2

Contents of main elements in the recovered CuSO₄, CoSO₄ and NiSO₄ products

Elements	Cu	Fe	Co	Ni	Mn	Li	Al	Zn
CuSO ₄ (%)	25.1	0.04	0.17	0.02	0.004	0.01	0.03	0.002
CoSO ₄ (%)	0.01	0.05	20.1	0.02	0.005	0.07	0.06	0.03
NiSO ₄ (%)	0.003	0.003	0.430	20.8	0.030	—	0.005	0.006

levels. A solution containing mostly Co²⁺ and Ni²⁺ was obtained. The extraction conditions for Co²⁺ and Ni²⁺ under different pH values were also investigated, and similar results with Zhang's and our previous studies (Zhang et al., 1998a,b; Nan et al., 2004, 2005) for this system could be obtained. Accordingly, Co²⁺ was extracted with 1 M Cyanex272 (10 wt.% saponification ratio) at 1:1 (O/A) phase ratio, using room temperature and 1 min of contact time; stripping was conducted with a 2 M H₂SO₄ solution at 1:1 (O/A) phase ratio, room temperature, and 1 min of contact time. It was found that over 97% recovery of Co²⁺ was approached at pH=5.1–5.3 after the target solution was separated with Cyanex272 twice and then the stripped solution subjected to extraction again. Subsequently, over 96% of Ni²⁺ was recovered as NiSO₄ through a similar treatment process when the pH value of the resulting solution was adjusted to 6.3–6.5, and Cyanex272 stripped of Co²⁺ was directly used as extractant.

The target sulfate salts were obtained after concentrating the final stripping solution. From the data presented in Table 2, it is indicated that the target resultants CuSO₄, CoSO₄ and NiSO₄ have a high purity, suggesting that these recovered products can be used as chemical materials directly. In addition, it was also shown that the extractants

Acorga M5640 and Cyanex272 could be recycled after stripping with H₂SO₄ solution, and the basic and acidic solutions produced in the course of the treatments could be reused or treated innocuously by mixing them together and then adjusting their pH values to neutral solution.

4. Conclusions

To sum up, an overall flow chart for reclaiming metal values from a mixture of spent LIBs and NiMH batteries based on a hydrometallurgical process is presented in Fig. 5.

The experimental results have demonstrated that over 94% metal values including RE, Co, Cu and Ni could be recovered from the mixture of spent LIBs and NiMH batteries under the proposed conditions. Acorga M5640 and Cyanex272 extractants could be recycled after stripping with sulfuric acid, which means the production cost would be decreased dramatically. The product CoSO₄ and NiSO₄ could be used as precursors to synthesize LiCoO₂ and Ni(OH)₂ electrode materials, proposing a possibility of cyclic use of metal values in LIBs and NiMH batteries. It is considered that the given process is environmentally acceptable and is applicable to a large-scale recycling treatment.

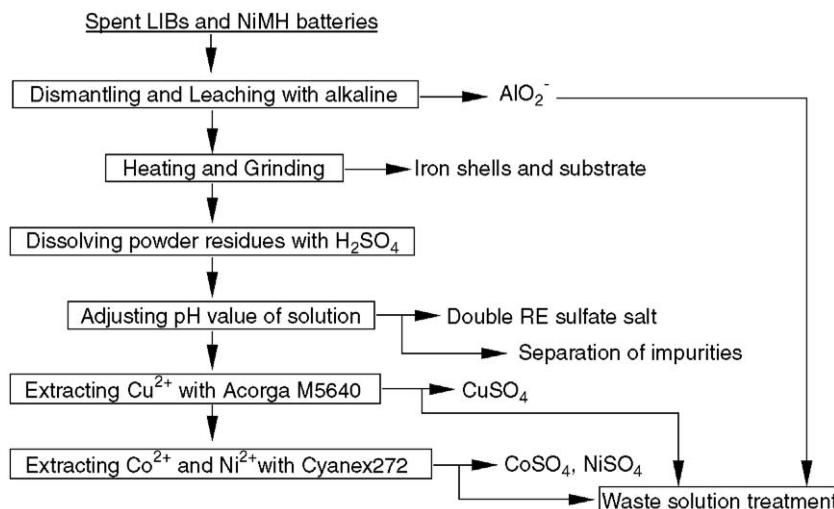


Fig. 5. Proposed flow chart for the recovery of metal values from the mixture of spent LIBs and NiMH batteries.

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References

- Alguacil, F.J., Cobo, A., Alonso, M., 2002. Copper separation from nitrate/nitric acid media using Acorga M5640 extractant: Part I. Solvent extraction study. *Chem. Eng. J.* 85, 259–263.
- Contestabile, M., Panero, S., Scrosati, B., 2001. A laboratory-scale lithium-ion battery recycling process. *J. Power Sources* 92, 65–69.
- Espinosa, D.C.R., Bernardes, A.M., Tenório, J.A.S., 2004. An overview on the current processes for the recycling of batteries. *J. Power Sources* 135, 311–319.
- Han, D.M., Nan, J.M., 2005. Advances on the recycling and reusing of spent batteries. *Chin. J. Power Sources* 29, 128–131 (in Chinese).
- Kim, D.S., Sohn, J.S., Lee, C.K., Lee, J.H., Han, K.S., Lee, Y.I., 2004. Simultaneous separation and renovation of lithium cobalt oxide from the cathode of spent lithium ion rechargeable batteries. *J. Power Sources* 132, 145–149.
- Kleinsorgen K., Kohler U., Bouvier A., Folzer A., 2000. Process for the recovery of metals from used nickel/metal/rare earth hydride storage batteries. US Patent 6110433.
- Köhler, U., Antonius, C., Bäuerlein, P., 2004. Advances in alkaline batteries. *J. Power Sources* 127, 42–45.
- Lee, C.K., Rhee, K.I., 2003. Reductive leaching of cathodic active materials from lithium ion battery wastes. *Hydrometallurgy* 68, 5–10.
- Lin J.R., Fan C., Chang I.L., Shiu J.Y., 2003. Clean process of recovering metals from waste lithium ion batteries. US Patent 65514311.
- Lupi, C., Pilone, D., 2002. Ni–MH spent batteries: a raw material to produce Ni–Co alloys. *Waste Manag.* 22, 871–874.
- Nan, J.M., Han, D.M., Cui, M., Zuo, X.X., 2004. Recycling of valuable metal from spent lithium ion batteries by solvent extraction. *China Battery Bimonthly*, vol. 34, pp. 309–311 (in Chinese).
- Nan, J.M., Han, D.M., Zuo, X.X., 2005. Recovery of metal values from spent lithium-ion batteries with chemical deposition and solvent extraction. *J. Power Sources* 152, 278–284.
- Nan, J.M., Han, D.M., Yang, M.J., Cui, M., 2006. Dismantling, recovery, and reuse of spent nickel-metal hydride batteries. *J. Electrochem. Soc.* 153 (1), A101–A105.
- Nishi, Y., 2001. Lithium ion secondary batteries; past 10 years and the future. *J. Power Sources* 100, 101–106.
- Pietrelli, L., Bellomo, B., Fontana, D., Montereali, M.R., 2002. Rare earths recovery from NiMH spent batteries. *Hydrometallurgy* 66, 135–139.
- Prickett O.G., Czajkowski R., Citta N.C., Klein M.R., Huston E.L., Galbraith P.W., 2001. Reclamation of active material from metal hydride electrochemical cells. US Patent 6180278.
- Tanii T., Tsuzuki S., Honmura S., Kamimura T., Sasaki K., Yabuki M., Nishida K., 2003. Method for crushing cell. US Patent 6524737.
- Wang, R., Yan, J., Zhou, Zh., Gao, X.P., Song, D.Y., Zhou, Z.X., 2002. Regeneration of hydrogen storage alloy in spent nickel-metal hydride batteries. *J. Alloys Compd.* 336, 237–241.
- Zhang, P.W., Yokoyama, T., Itabashi, O., Suzuki, T.M., Inoue, K., 1998a. Hydrometallurgical process for recovery of metal values from spent lithium-ion secondary batteries. *Hydrometallurgy* 47, 259–271.
- Zhang, P.W., Yokoyama, T., Itabashi, O., Wakui, Y., Suzuki, T.M., Inoue, K., 1998b. Hydrometallurgical process for recovery of metal values from spent nickel metal hydride secondary batteries. *Hydrometallurgy* 50, 61–75.
- Zhang, P.W., Yokoyama, T., Toshiro, O., Wakui, Y., Suzuki, T.M., Inoue, K., 1999. Recovery of metal values from spent nickel-metal hydride rechargeable batteries. *J. Power Sources* 77, 116–122.